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ARTICLE TYPE

Mesoporous titania microspheres composed of exposed active faceted nanosheets and their catalytic activities for solvent-free synthesis of azoxybenzenes

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Mesoporous titania microspheres composed of nanosheets with exposed active facets were prepared by hydrothermal synthesis in the presence of hexafluorosilicic acid. They exhibited superior catalytic activity in the solvent-free synthesis of azoxybenzene by oxidation of aniline and could be used for 7 cycles with slight loss of activity.

Titanium dioxide (TiO_2) has been intensively investigated in the last couple of decades since its relative low cost and widely application in many areas such as photocatalysis, energy conversion and storage, sensor, catalyst, and catalyst support.[1] It is generally synthesized as nanoparticles and nano/microspheres. TiO_2 with other morphologies, such as disks,[2] rods,[3] wires[4] and tubes,[5] is also produced, as these morphologies can endow unique properties of TiO_2. Recently, TiO_2 with highly exposed crystal facets and with these exposed facet crystal-constructed hierarchical structures has attracted much attention. Various techniques are developed to prepare these kinds of TiO_2, mainly by hydrothermal or solvothermal treatment of titanium precursor solutions synthesis in the presence of fluoric ion[6,7] and capping reagents such as ammonia,[8] H_2O_2,[9] alcohols,[10] etc, or by hydrothermal treatment of titania podwer, nanowires or nanotubes in acid/basic solutions.[11] Further results denmonstrate that expose of {001}, {110}, {010}, {111}, {102}, {106} and {103} facets can enhance the reactivity of TiO_2, especially in photocatalysis and dye-sensitive solar cells (DSSCs).[12] Similarly, TiO_2 with the exposed facet crystal-constructed V-shaped channels,[13] nanosheets or nanorods assembly,[14,15] core-shell,[16] sphere-in-sphere,[17] and dandelion-like[18] hierarchical structures exhibit outstanding performance in DSSCs, lithium ion batteries, and photocatalysis.

As a versatile catalytic material, TiO_2 is mostly used as photocatalysts and a support of both metal and oxide catalysts in heterogeneous catalysis. A few work use nano-sized TiO_2 as heterogeneous catalysts mainly for organic synthesis, such as Michael addition of indoles to a,b-unsaturated ketones,[19] Mannich synthesis of β-aminocarbonyls,[20] synthesis of substitude 2-oxodihydropyrroles and bis(indolyl)methanes,[21] etc. It is interesting that there are limited work on use TiO_2 as a catalyst for catalytic oxidation reactions, although titanium containing materials, such as titanium-substituted molecular sieves,[22] are good catalysts for this kind of reaction. Oxidations of amines with H_2O_2 to oximes and azoxybenzenes are the main two reactions reported so far using the nano-sized TiO_2 as the catalysts in which solvents such as acetone, CH_3CN, CH_3OH, etc, are used to achieve good yields.[23,24] It would be of both academic and industrial interest to examine the catalytic oxidation activity of these TiO_2 with highly exposed crystal facets or with hierarchical structures.

Aromatic azo compounds are high-value intermediates for production of dyes, pigments, food additives, and drugs.[25] Reduction of nitroaromatics and oxidation of anilines are the main route to prepare these compounds. Oxidation of anilines can be carried out with oxygen at high pressures or H_2O_2 under mild conditions. From a practical viewpoint, a mild reaction is more favorable. As mentioned above, nano-sized TiO_2 exhibits excellent catalytic activity in oxidation anilines to azoxybenzenes, however, a solvent has to be used. Synthesis of azoxybenzene by oxidation of aniline with H_2O_2 without a solvent provides a green and mild route and needs to be developed.

Herein, we reported preparation of mesoporous TiO_2 microspheres (MTMs) with particle size of 2-15 μm composed of TiO_2 nanosheets (side length of 10-20 nm, thickness of 4-6 nm) with exposed {101} facet (56%) by a simple hydrothermal synthesis. The microspheres exhibited superior catalytic activities in solvent-free oxidation of arylamines to azoxybenzenes rather than azobenzene. To the best of our knowledge, no such application of exposed facet crystal-constructed hierarchical TiO_2 structures in heterogeneous catalysis has been reported.

The MTMs were hydrothermally synthesized at 180 °C for 48 h using a synthesis solution with a molar ratio of 1TBOT: $0.1H_2SiF_6$: $1.5H_2O$ prepared by adding a H_2SiF_6 aqueous solution into TBOT under vigorous strirring (ESI†). Fig.1a shows XRD patterns of the as-synthesized sample, indicating formation of pure anatase TiO_2 (tetragonal, *I*41/*amd*, JCPDS No. 21-1272). The diffraction peaks at 2θ of 25.3°, 37.8°, and 48.5° can be observed obviously, corresponding to (101), (004) and (200) faces of TiO_2. The peak intensity at 2θ=25.3° is much stronger than those at 37.8° and 48.5°, implying the preferred growth along (101) face.[26] The primary crystallite size calculated from the (101) peak of XRD pattern using the

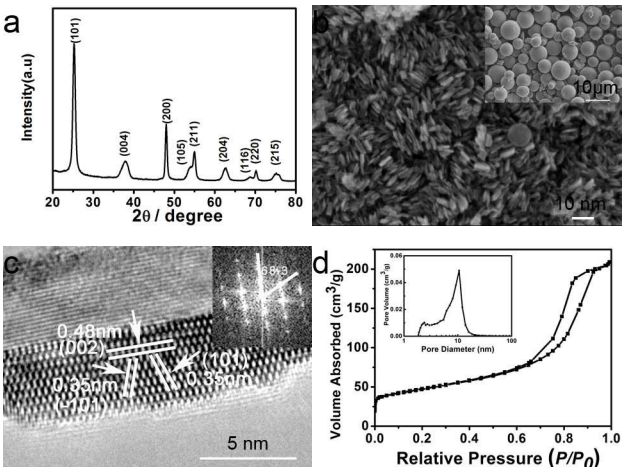


Fig. 1 XRD pattern (a), SEM images (b), TEM image (c) of the TiO2 microspheres composed of nanosheets, recorded from anatase single nanocrystal with the corresponding fast-Fourier transform (FFT) pattern in the inset, and nitrogen adsorption-desorption isotherm and Barret-Joyner-Halenda (BJH) pore size distribution plot of the MTM (d).

scherrer equation is about 14.7 nm. XRD patterns of the samples synthesized at 2-96 h (Fig. S1, ESI†) indicate that the intensity of the (101) face becomes stronger with increasing the synthesis time and reaches the strongest at 48 h, indicating the highest crystallinity of the sample after synthesis for 48 h. Fig. 1b show SEM picture of the MTM. It exhibits spherical morphology with particle size of 2-12 μm (Inset in Fig. 1b). Close observations reveals that the microsphere is composed of compactly packed nanocrystals.

To elucidate the fine structure of nano-sized sheets, we examined the sample by TEM after grounding and ultrasound dispersing the sample. A representative high-resolution TEM image of a single nanosheet (Fig. 1c)[27] reveals that these nanosheets are well-faceted nanocrystals with side length of 10-20 nm and thickness of *ca.* 4.6 nm. The (-101), (101) and (002) atomic planes with lattice spacings of 0.35, 0.35 and 0.48 nm indicate that the top/bottom surface exposed by truncation is bound by a {001} facet.[28,29] The inset of Fig. 1c shows that the angle labeled in the corresponding fast-Fourier transform (FFT) image is 68.3±0.3°, which is identical to the theoretical value for the angle between the {101} and {001} facets.[28] These facets prove that the anatase single crystals exhibit flat facets of {101} and {001}. On the basis of the above structural information, the percentage of {001} facets in the TiO_2 nanosheets shown in Fig. 1c is estimated to be 44% according to eq. 1.[30] Correspondingly, the percentage of {101} is 56%.

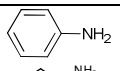
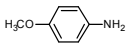
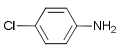
$$\frac{a^2}{\frac{(b^2-a^2)}{\cos\theta}+a^2}\times 100\% \qquad (1)$$

Where, a is the side length of {001} facet, b the bottom edge of {101} facet and θ the value for the angle between the {101} and {001} facets.

The nitrogen adsorption-desorption isotherm was measured to determine the specific area and pore volume of the MTM. The corresponding results were presented in Fig. 1d. The pore size distribution, derived from desorption data and calculated using the BJH model, indicated that the average pore of such a sample is around 10.2 nm. The Brunauer–Emmett–Teller (BET) specific surface area of the sample calculated from N_2 adsorption is 117 m^2 g^{-1}, which is larger than those of conventionally prepared TiO_2 microsphere.[13,15] The much higher BET surface area of the MSM may provide the possibility of contacting active center more effectively.

To investigate the elemental compositions and the binding states of the MTM, the sample was analyzed by XPS (Fig. S3, ESI†). Sharp photoelectron peaks appear at binding energies of 458 (Ti 2p) and 531 eV (O 1s). The F 1s peak at 684.5 eV is observed due to surface fluorination. High-resolution XPS was used to detect the surface F 1s, Ti 2p, and O 1s core levels. No signals for F^- in the lattice (BE =688.5 eV) is found after the MTM was calcined at 600 °C, implying that all F^- is physically adsorbed on the surface of the MTM, and does not substitute of oxygen in TiO_2 lattice. The binding energy of Ti 2p3/2 equals to 458.7 eV and the binding energy of Ti 2p1/2 equals to 464.4 eV, which are identical to the reported literature.[31] These results confirm that titanium exists as Ti (IV) state. The O 1s peak at 530.2 eV indicates oxygen in Ti–O–Ti. No Si peak (101.8 eV) is observed, suggesting that Si in H_2SiF_6 does not enter into or adsorb on the MTM.

Table 1 Oxidation of arylamines to azoxybenzenes in the presence of TiO2/H_2O_2 system.

Entry	Arylamine	Time (h)	Conversion (%)	Yeild (%)
1		0.75	97.8	95.6
2		2	98.7	94.5
3		4.5	91.0	86.5
4		4.5	85.4	81.3
5		6.0	80.8	75

(catalyst =25 mg; arylamines=0.02 mol; arylamines/H_2O_2 molar ratio=1: 1.7; temperature=333 K)

The MTM shows quite high catalytic activity in the catalytic oxidation of arylmines with H_2O_2 to azoxybenzenes. In particular, no solvent is used in these reaction systems, unlike the reported system for conversion of aniline H_2O_2 to azoxybenzene, in which acetone, CH_3CN, CH_3OH, are usually used as solvent,[23,24] implying a green catalytic synthesis route. Table 1 listed the reaction results of oxidation of some arylamines with H_2O_2. It is observed from that aniline results in a good yield of azoxybenzene within a shorter reaction when compared with the substituted anilines, while toluidines are more reactive than the chloro or methoxy substituted anilines. This may be attributed to the smaller size of toluidine atoms, which would allow the reactant molecules to gain closer proximity to the active centers on the titanium peroxo species compared to the larger chlorine atoms or methoxy groups. However, the differences in the reactivity of various substituted anilines are dependent on the synergetic

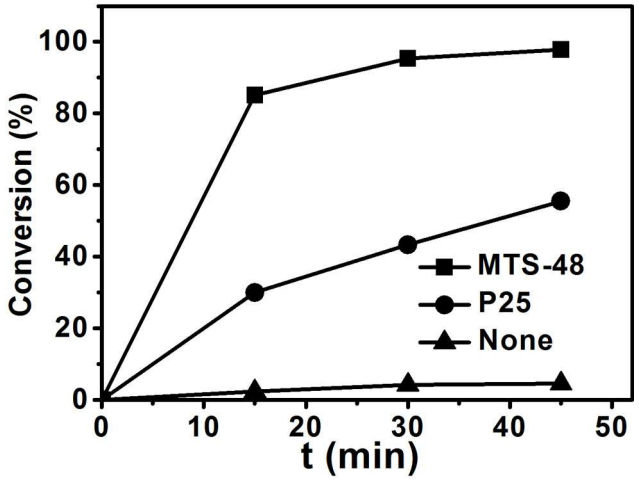


Fig. 2 Effect of reaction time on aniline conversion and azoxybenzene yield with MTM and P25 and without a catalyst. (catalyst =25mg; aniline=1.86 g; aniline/H_2O_2 molar ratio=1:1.7; temperature=333 K)

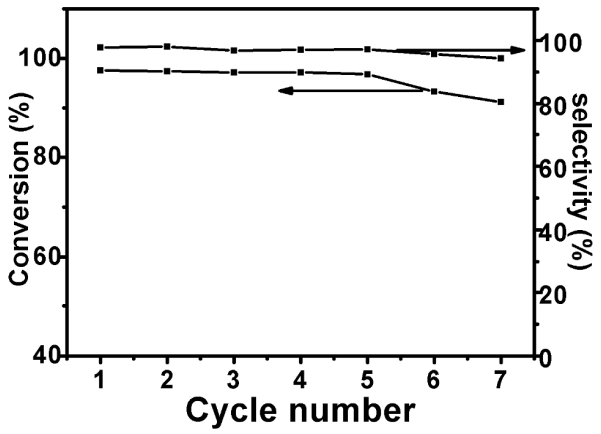


Fig. 3 Cycling curve for aniline oxidation with the MTM as the catalyst.

effect of the molecular parameters such as mesomeric (+M), inductive (+I/-I) and the steric effect of the substituents.[24] Furthermore, it should be noted that no obvious difference was observed on the conversion of aniline and the yield of azoxybenzene when the reaction was conducted with or without sun light irradiation, clearly suggesting that MTM does not act as a photocatalyst in the present reaction.

To compare the catalytic property of the TiO_2 microspheres with TiO_2 powder P25 (Degussa), we conducted time-dependent kinetics of aniline with H_2O_2 using the MTM and P25 as the catalysts. Blank test without a catalyst was also conducted. The reaction results shown in Fig. 2 clearly demonstrate that this reaction goes on a quite slow reaction rate with low conversion of aniline without a catalyst. Increasing the reaction time directly increases the aniline conversion using the MTM and P25. The reaction rate of the MTM is significantly greater than that of P25. The yield of azoxybenzene increases smoothly with the reaction time for 30 min to 45 min. After 45 min, the aniline conversion reaches a maximum value of 97.8% and the yield of azoxybenzene is up to 95.6%, which are much higher than those by P25.

Fig. 3 shows that after 6 recycling uses, the activity of the MTM remains above 93.3% with selectivity of azoxybenzene being 95.6% , which indicates that the exposed crystal-facets TiO_2 microspheres have high catalytic stability in the oxidation of arylamine. A slight loss of the catalytic activity was observed in the 7th recycling use (conversion: 91.2%, selectivity: 94.3%).

To identify the contributions of the {101} facets and hierarchical structure of the MTM on the aniline oxidation, diverse samples with varying percentages of exposed {101} facets were prepared by changing the synthesis time, and the results of aniline oxidation to azoxybenzene on these samples were listed in Table 2 (Entries 1 and 2). By extending the synthesis time to 72 and 96 h at 180 °C, the percentages of {101} facets of the MTM are 47% to 37%, respectively. This is similar to the result reported by Yang, et al.[6a]. The conversion of aniline and the yield of azoxybenzene are slightly decreased, suggesting possibly more active sites on the MTM with higher percentage of {101} facet. To examine the effect of hierarchical structure of the MTM on the aniline oxidation, we ground the MTM sample to form mostly nanosheets. Even with an increase in the percentage of {101} facet (56%), the conversion still decreases slightly (entry 3), possibly due to lack of hierarchical structure. To further elucidate the effect, the anatase TiO_2 nanosheet-based microspheres (ATNM)[15] and anatase TiO_2 nanoparticle-based hierarchical spheres (ATNHS)[29], as well as titania nanosheets (NS)[7] were also prepared, with the {101} facet percentage of 94%, 10%, and 20%, respectively. The results indicated that the samples with hierarchical structures and both very high or low {101} facet percentage (entries 4 and 5) exhibit quite low conversions and yields, while the sample with vey low {101} facet percentage shows slightly low conversion and yield (entry 6), compared with those for the MTM. These results suggested that both the {101} facet percentage and the hierarchical structure of the MTM play significant roles in oxidation of aniline. To obtain much higher catalytic activity, TiO_2 catalysts with mediate {101} facet percentages as well as the hierarchical structure have to be used (entries 1 and 2 in Table 2).

Table 2 Oxidation of aniline to azoxybenzene at different catalyst

Entry	Catalyst	Conversion (%)	Yeild (%)	P(101) %	hierarchical structure
1	MTM[a]	94.5	90.9	47	yes
2	MTM[b]	93.6	89.6	37	yes
3	MTM[c]	91.4	89.3	56	no
4	ATNM	22.6	21.0	94	yes
5	ATNHS	61.8	58.4	10	yes
6	NS	87.3	85.4	20	no

[a] The MTM sample synthesized at 180 °C for 72 h; [b] The MTM sample synthesized at 180 °C for 96 h; [c] The MTM sample synthesized at 180 °C for 48 h and ground into mostly nanosheets. The reaction time is 0.75 h.

In conclusion, we developed a new approach to synthesize anatase mesoporous TiO_2 microsphere composed of nanosheets with exposed {101} facet (56%) by a simple hydrothermal synthesis using H_2SiF_6. The microsphere shows high conversion and yield in oxidation of arylamines to azoxybenzenes with H_2O_2 without a solvent at mild conditions. Both the appropriate proportion of {101} and

{001} facets and the hierarchical structure of the MTM contribute the high reaction activity. The MTM provides an enviroment-friendly and easily recyclable heterogeneous catalytic route for the preparation of azoxybenzene.

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† Electronic Supplementary Information (ESI) available: Experimental Detail, XRD pattern, XPS spectra. See DOI: 10.1039/b000000x/

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